

(PDMS) elastomer, was purchased from Essex Brownell (Edison, N.J.). For all devices a 10:1 (by weight) mixture of PDMS base/curing agent was used and was degassed under vacuum and cured at 70° C. for ~24 hours. The reagents $\text{Fe}(\text{CN})_6^{4-}$ ($\text{Fe}(\text{II})$), $\text{Cr}_2\text{O}_7^{2-}$ ($\text{Cr}(\text{VI})$), I^- , $\text{S}_2\text{O}_8^{2-}$, KCl, and HCl were obtained from Sigma-Aldrich Co. (St. Louis, Mo.) and used as received; solutions of these reagents were made in 18 M Ω water. All other chemicals were purchased from Sigma-Aldrich Co. and used as received unless indicated otherwise.

[0135] Channels that were 50 μm high and had various structures (e.g., herringbone) on the top walls of the channels that were also 50 μm high were fabricated in PDMS by replicating a master obtained by conventional photolithography. The SU-8 channel structure on the master was prepared on a silicon wafer by a two-step photolithographic process. The channels were embedded in PDMS and were aligned to a glass slide bearing platinum electrodes under an optical microscope. The device was sealed by using clamps that applied a small pressure to the device. The PDMS slab and the glass slide were sealed reversibly; this reversible seal allowed reuse of the glass slide bearing the electrodes several (~5) times.

[0136] Electrodes were fabricated as follows: Microscope slides (75×50×1 mm, borosilicate glass, Corning, N.Y.) were used as supports for the electrodes and to close the channels embedded in PDMS. To fabricate the electrodes, the glass slides were first cleaned (using water and ethanol) and then treated with hexamethyldisilazane (Microelectronics Materials Corp.) to promote the adhesion of the Shipley 1813 photoresist (Microchem Corp.). Photoresist was spin-coated at 500 rpm for 5 s and at 4500 rpm for an additional 30 s to give a thickness of ~1.2 μm . The slides were then placed directly on a digital hotplate set at 105° C., baked for 3 min, and promptly removed. A computer-aided design (CAD) program was used to design the shape of the electrodes; this design was printed onto a transparency film (PageWorks, Cambridge Mass.), which served as a photomask for photolithography. The photomasks were placed on top of the resists, and the resists were exposed to UV light for 6 s at 50 mJ s⁻¹. The resists were then immersed in fresh 351 developer (Microchem Corp., composition 80% NaOH and 20% H₂O) with agitation from a Branson 251 sonifier (VWR Corp.). Within 1 min, the exposed regions began to exude a red color, indicating that development of the photoresist had begun. The agitation was continued until formation of the red color ceased and the resulting pattern attained a uniform appearance (~30 s). After rinsing the slides thoroughly with 18 M Ω water, they were dried under a stream of N₂. 7.5 nm of titanium (to promote adhesion) was evaporated sequentially with 200 nm of Pt onto the patterned slides using an electron beam evaporator. The remaining photoresist was removed by immersing the slides in an acetone (or ethanol) bath and then sonicating them. Peeling off the photoresist revealed the metallic patterns formed on the slides that were to be used as electrodes.

[0137] Alignment of the electrodes and microfluidic channels is shown in FIG. 4A. Since all of the electrodes (except for the first) cross under several channels of the system, the electrodes needed insulation from all of the channels except one, where detection takes place. Each electrode was arranged to detect the solution in the right-most channel crossing over the electrode. In each of these positions, a

small aperture (100 μm ×100 μm) in a thin layer of photoresist allowed contact between the electrode and the solution flowing in the channel above it. To make this insulating layer, a thin layer (~10 μm) of SU 8-2005 photoresist (Microchem Corp.) was spun (5 s at 500 rpm and 15 s at 900 rpm) on the glass bearing the electrodes. A photomask having the pattern of the apertures on top of the electrodes was aligned and exposed system to UV light. The resist was developed in a propylene glycol methyl ether acetate (PGMEA) bath for 2 mins, leaving the apertures (100×100×10 μm , lwh) in the resist.

[0138] One of the platinum microelectrodes was converted to a reference Ag/AgCl electrode by applying a potential difference of 800 mV between the Pt integrated microelectrode and an external Pt macroelectrode. The electrodes were immersed in a solution of commercial silver bath (Techni-Silver EHS-3, Technic Inc.) and the Pt microelectrode was polarized as a cathode in order to electroplate Ag on the Pt. Then, after immersing the electrodes into a saturated KCl solution, a potential difference of 800 mV was applied for ~15 s to the electrodes (the newly formed Ag/Pt electrode polarized anodically), in order to form an AgCl layer (~100 nm in thickness).

[0139] To perform the experiments, solutions of titrant and sample were placed in 5 mL syringes (Becton, Dickinson and Co.) without the plunger; these syringes were used as reservoirs. These syringes were attached to polyethylene tubing (Intramedic, PE 20) that connected to the inlets of the device. The solutions were allowed to flow by gravity. The flow rate of each solution was adjusted by changing the height of each reservoir. The relative flow rates of the solutions in the inlets were calibrated to obtain 1:1 splitting at each junction by viewing the splitting under an optical microscope. Flow rates were measured at the outlet (waste) by weighing the amount of solution recovered at the end of the device during a fixed period of time.

[0140] A difference in potential between a Pt electrode located in one of the channels and the Ag/AgCl reference electrode was measured using a Fluke 75 Multimeter. One Pt electrode was connected to the voltmeter, the measurement was taken, the electrode disconnected and then the adjacent one was connected. The measurements can be detected simultaneously by connecting the electrodes of a device to a connector block (e.g., TBX-68 I/O, National Instruments), which sends electronic signals to a data acquisition card (e.g., PCI card) that connects to a computer. The signals can be read by a software program such as LabVIEW (National Instruments).

Example 6

[0141] One of the fabricated devices is shown in FIG. 26 and was used to characterize the efficiency of mixing using electrochemical tools.

[0142] A potentiometric titration between an oxidant and a reductant may proceed faster when an efficient mixing of the two solutions occurs. In microfluidic channels, mixing of two solutions may be slow due to the laminar behavior of the flow. The use of a chaotic advective mixer (CAM) using a ribbed microstructure in the flow channel may aid in mixing.

[0143] As shown in FIG. 26, a CAM 310 forms part of a microfluidic device that was used to evaluate titration effi-